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PROBLEM DEFINITION STUDIES ON POTENTIAL ENVIRONMENTAL POLLUTANTS

VI. PRELIMINARY ASSESSMENT OF ENVIRONMENTAL EFFECTS OF SEVEN SUBSTANCES USED IN PYROTECHNIC COMPOSITIONS AT PINE BLUFF ARSENAL

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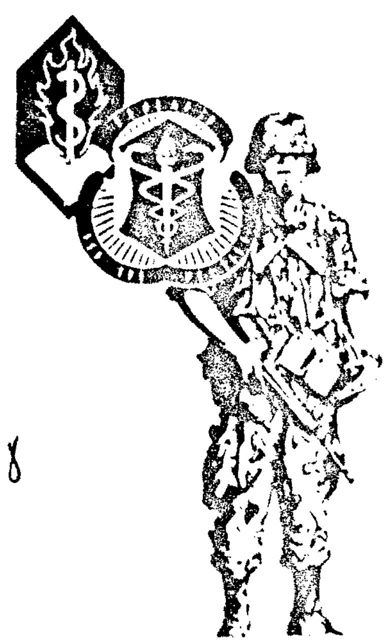

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Procurement data for the period 1965-1975 are used to estimate soil contamination by pyrotechnic and smoke chemicals at Pine Bluff Arsenal, AR, during this 11-year period.

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PREFACE

The body of this technical report is essentially a verbatim reissue of Memorandum Report 28-79, dated 27 November 1979. It is reproduced here to make it available to general readers through the Defense Technical Information Center. David R. Cogley was retained under U.S. Army Medical Research and Development Command contract DAMD17-77-C-7050, Walden Division of Abcor, Inc., Wilmington, MA.

INTRODUCTION

The U.S. Army Toxic and Hazardous Materials Agency, formerly the Office of the Project Manager for Chemical Demilitarization and Installation Restoration, has identified an initial list of substances (Table 1) requiring assessment because of their historical presence at Pine Bluff Arsenal (PBA), Arkansas and their potential presence outside the boundaries of the arsenal.[1] Prior to initiating this problem definition study, careful consideration was given to each substance and a revised list (Table 1) was developed.

TABLE 1. INITIAL AND REVISED LISTS OF POLLUTANTS AT PINE BLUFF ARSENAL

Substance	Initial list	Revised list
DDT	X	
Thiodiglycol	X	
Phosphorus (white)	X	
Auramine	X	X
Benzanthrone	X	X
1,4-Di-p-toluidinoanthraquinone	X	X
1,4-Diamino-2,3-dihydroanthraquinone	X	X
1-Methylaminoanthraquinone	X	X
Vat Yellow 4		X
Hexachloroethane		X

DDT, for which there is an abundance of data in the published literature, is the subject of an ongoing restoration program and is considered to be a separate problem; therefore, DDT and its analogs are treated in a separate report.[2] Thiodiglycol and white phosphorus have already been assessed in technical reports of the U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL)[3-6]. From information obtained during a site visit to PBA,[7] two substances, Vat Yellow 4 and hexachloroethane (a component of white smoke) were added to the revised list. It has been learned that Vat Yellow 4 was substituted for auramine hydrochloride in yellow smoke grenades in 1961.[8]

The objective of the present report is to summarize available data on the environmental effects of the seven substances in the revised list at PBA. Physical, chemical, toxicological, and biological data for these substances are presented in a separate USAMBRDL technical report.[9] A detailed description of PBA and its watershed, history of contamination, sampling efforts, chemical analysis data, and stream survey data are presented in a technical report of the Chemical Systems Laboratory.[10]

UTILIZATION OF PYROTECHNIC SUBSTANCES AT PINE BLUFF ARSENAL

Most of the pyrotechnic materials have been used to produce smoke grenades. A typical grenade contains 330 g of grenade mix, composed of 40% dye mix, 25% each sodium bicarbonate and potassium chlorate, and 10% sulfur. A single production line at PBA is capable of producing 8,000 grenades per day. The regular practice has been to operate a single line at capacity until the required number of grenades of a particular smoke color is produced.

Procurement data for pyrotechnic materials for an 11 year period through 1975 are presented in Table 2.[11] (No prior year data are available.) These materials are purchased mainly as mixes, the compositions of which are given in Table 3. Table 4 gives the minimum chemical requirements for dyes used in preparing dye mixes. Table 5 lists yearly shipments of dyestuff on a 100% pure basis, estimated from the data of Tables 2, 3 and 4. It will be noted that unknown constituents make up a significant fraction of these materials. Military specifications provide no clue to the identity of unknown constituents, but it may be surmised that they are organic impurities closely related to the specified dyes and/or diluents, such as starch. Table 6 provides procurement data for hexachloroethane.

TABLE 2. PYROTECHNIC MATERIALS RECEIVED BY PBA, 1965-75[a]

Year	Shipment, 1000 lb					
	Benzanthrone[b]	Red mix	Yellow dye	Yellow mix	Green mix	Violet mix
1965	13.7	19.1	7.1	--	34.8	33.8
1966	10.8	449.9	81.8	--	108.0	102.8
1967	137.2	125.0	--	229.2	462.8	--
1968	--	78.4	--	265.6	114.8	--
1969	2.5	24.0	2.0	--	--	--
1970	--	103.0	38.0	81.5	15.0	47.0
1971	--	115.0	80.3	25.0	99.7	90.2
1972	--	38.5	--	111.8	45.8	73.0
1973	--	35.0	--	40.0	40.0	32.9
1974	--	--	--	77.5	--	--
1975	--	19.9	--	15.2	46.1	--

a. Ref.11; b. Technical grade.

TABLE 3. ESTIMATED PERCENT COMPOSITION OF DYE MIXES

Mix	Composition, percent					
	Benzanthrone	Red dye	Yellow dye	Green dye	Violet dye	Dextrin
Red	--	85	--	--	--	15
Yellow[a]	65	--	35	--	--	--
Green[a]	20	--	10	70	--	--
Violet	--	20	--	--	80	--

a. Mil.Spec. not given.

TABLE 4. COMPOSITION OF PYROTECHNIC AGENTS

Agent	Major component	Percent	Other	Percent
Benzanthrone	Benzanthrone	77	Hydrocarbon oil	2
Red Dye	Disperse Red 9[a]	90		
Yellow Dye	Vat Yellow 4[b]	80		
Green Dye	Solvent Green 3[c]	90		
Violet Dye	1,4-diamino-2,3-dihydroanthraquinone	70		

a. 1-Methylaminoanthraquinone; b. Dibenzo[b,def]chrysene-7,14-dione;
c. 1,4-Di-p-toluidinoanthraquinone.

TABLE 5. PYROTECHNIC DYES RECEIVED BY PBA, 100% BASIS[a]

Year	Dye Shipments, 1000 lb (pure)				
	Benzanthrone	Red[b]	Yellow[c]	Green[d]	Violet[e]
1965	15.9	20.6	8.5	22.0	18.9
1966	25.0	362.6	74.1	68.0	57.5
1967	291.7	95.6	101.2	291.5	0
1968	150.6	60.0	83.5	72.3	0
1969	1.9	18.3	1.6	0	0
1970	43.1	87.3	54.5	9.4	26.3
1971	27.9	104.3	79.7	62.8	50.5
1972	63.0	42.6	35.0	28.9	40.9
1973	26.2	32.7	14.4	25.2	18.4
1974	38.8	0	21.7	0	0
1975	14.7	15.2	8.0	29.0	0
11-yr. av.	63.5	76.3	43.8	35.4	19.3

a. Derived from Tables 2-4; b. 1-Methylaminoanthraquinone; c. Vat Yellow 4; d. 1,4-Di-p-toluidinoanthraquinone; e. 1,4-Diamino-2,3-dihydroanthraquinone.

TABLE 6. HEXACHLOROETHANE SHIPMENTS RECEIVED BY PBA, LB[a]

1966	572,000
1967	629,000
1972	128,000
1973	160,000
1975	137,000
1976	662,000

a. Ref. 11.

WASTE AND WASTEWATER CONSIDERATIONS

Water is used in the production of grenades for dust suppression, fire protection, and periodic cleanup. During a site visit by USAMBRDL personnel, PBA personnel estimated that roughly 50 lb of grenade mix, or about 1 percent of the total, was carried off each day in the waste stream.[12] The water is carried from the production area in shallow ditches which drain into a low area, eventually discharging into the Arkansas River. Since the dyes are essentially insoluble in water, most of the transport is mechanical. Some build-up of dyes in the vicinity of the production facility is evident. In a nearby test facility, 40 or more grenades are ignited each day during production. In March 1976 the test facility, an open basement, was abcut half filled with empty canisters, but there was no apparent build-up of dyes on structures, vegetation, or soil in the immediate vicinity. It is not known whether this facility is a significant source of contamination.

For estimation of potential soil contamination, it is assumed that all dye substances delivered to PBA were used in manufacture of smoke grenades during the interval 1965 to 1975. Table 7 presents estimated pyrotechnic wastes for this 11 year period which, since it includes the Vietnam war era, probably accounts for almost all of the contamination from pyrotechnics over the past 25 years. It should be noted that Table 7 does not account for starter mix, a solution containing sulfur, cornstarch, and potassium chlorate, which is added at a late step in grenade production.

TABLE 7. TOTAL AND ESTIMATED WASTE PYROTECHNIC CHEMICALS AT PBA, 1965-75

Chemical[a]	Consumption,[b] lb	Waste,[c] lb
Benzanthrone, pure	699,000	7,000
Red dye, pure	839,000	8,400
Yellow dye, pure	482,000	4,800
Green dye, pure	609,000	6,100
Violet dye, pure	212,000	2,100
Sodium bicarbonate	2,234,000	22,300
Potassium chlorate	2,234,000	22,300
Sulfur	893,000	8,900
Dextrin	151,000	1,500
Oil	18,000	180
Unknown	563,000	5,600

a. Calculations are based on pure chemicals; b. Grenade composition assumed to be 40 percent dye mix, 25 percent each sodium bicarbonate and potassium chlorate and 10 percent sulfur (starter mix is not included); c. 1 percent of total mix is assumed wasted.

Since little is known concerning the biodegradability, environmental chemistry, or soil translocation of the pyrotechnic dyestuffs, it is not productive to speculate on the fate of these materials. The non-dye constituents, though not intentionally addressed in this study, are readily accounted for. Sodium bicarbonate would disappear into the immense environmental carbonate pool; potassium chlorate retains its phytotoxicity for several years when applied to land for weed control but otherwise presents little environmental hazard;[4] sulfur, essentially harmless in itself, slowly degrades chemically and biochemically to nontoxic products; dextrin (a starch derivative used in foods and pharmaceuticals) and oil are readily degradable. Unknown materials constitute about 6 percent of the total wastes.

SAMPLING RESULTS

Bender et al. report that in May, 1977, 10 sediment samples were obtained from each of 22 sites at PBA.[10] Samples from sites known to be potentially contaminated with dyes were chemically analyzed for four dyes. Detection limits were: red dye, 6.4 ppm; yellow dye, 11.0 ppm; green dye, 15.0 ppm; and benzanthrone, 12.0 ppm. Dyes were not detected at the stated levels in the samples analyzed. It should be noted, however, that the pyrotechnic dyes may be readily converted to other colored compounds or leuco (colorless) dyes which may present greater toxic hazards and would not have been detected. For example, 1,4-diamino-2,3-dihydroanthraquinone (violet dye) is only weakly mutagenic, while two potential environmental transformation products, 1,4-diaminoanthraquinone and 1,4-dihydroxyanthraquinone are strongly mutagenic by the Ames test.[13]

CONCLUSION

There is, at present, no evidence for a negative impact of dyes on the PBA environment or the ecology of PBA. Sampling and chemical analysis have demonstrated that if the dyes are present, they are present at concentrations below approximately 10 ppm. Though not discussed in this context, the data of Bender et al. tend to indicate that species diversity is high (i.e., ecological impacts are low) in areas possibly contaminated by dyes. Though the data available to the authors do not indicate any serious impacts of dyes on the wildlife populations studied, it may not be concluded that serious food-chain associated impacts to humans are necessarily absent.

REFERENCES

1. Letter, AMCPM1-DRR, 1 Dec 75, subject: Installation Restoration Directed Actions.

2. Burrows, W.D., D.R. Cogley, W.G. Light, J.C. Dacre, and G. Woodard. 1979. "Problem definition studies on potential environmental pollutants. VII. Physical, chemical, toxicological, and biological properties of DDT and its derivatives." Technical Report 7906, AD A094236. U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

3. Rosenblatt, D.H., T.A. Miller, J.C. Dacre, I. Muul, and D.R. Cogley. 1975. "Problem definition studies on potential environmental pollutants: I. Toxicology and ecological Hazards of 16 substances at Rocky Mountain Arsenal." Technical Report 7508, AD B039661. U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

4. Rosenblatt, D.H., T.A. Miller, J.C. Dacre, I. Muul and D.R. Cogley. 1975. "Problem definition studies on potential environmental pollutants: II. Physical, chemical, toxicological, and biological properties of 16 substances." Technical Report 7509, AD A030428. U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

5 . Rosenblatt, D.H., M.J. Small, and J.J. Barkley, Jr. 1973. "Munitions production products of potential concern as waterborne pollutants -- phase I." Technical Report 7307, AD 912752. U.S. Army Medical Environmental Engineering Research Unit, Edgewood Arsenal, MD.

6. Dacre, J.C. and D.H. Rosenblatt. 1974. "Mammalian toxicology and toxicity to aquatic organisms of four important types of waterborne munitions pollutants -- an Extensive literature evaluation." Technical Report 7403, AD 778725. U.S. Army Medical Bioengineering Research and Development Laboratory, Aberdeen Proving Ground, MD.

7. Dacre, J.C., "Report of visit, Pine Bluff Arsenal, 11-12 March 1976" (April 1976).

8. Letter, SAREA-DM, 14 Oct 76, subject: Installation Restoration Directed Actions.

9. Dacre, J.C., W.D. Burrows, C.W.R. Wade, A.F. Hegyeli, T.A. Miller, and D.R. Cogley. 1979. "Problem definition studies on potential environmental pollutants. V. Physical, chemical, toxicological, and biological properties of seven chemicals Used in pyrotechnic compositions." Technical Report 7704, AD A090631. U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.

10. Bender, E.S., P.F. Robinson, A.E. Asaki, R.J. Donald, D.R. Rieder, V.J. Kelmeckis, and L.C. Bates. 1978. "The effects of wastewater emissions and nonpoint discharges on water quality and aquatic macroinvertebrate communities at Pine Bluff Arsenal, Pine Bluff, Arkansas." ARCSL-TR-78062. Chemical Systems Laboratory, Aberdeen Proving Ground, MD.

11. Data provided by Army Procurement Office, Edgewood Arsenal, MD, 1976.

12. Aikman, L., Pine Bluff Arsenal, personal communication to W.D. Burrows, 11 Mar 1976.

13. Brown, J.P., and R.J. Brown. 1976. "Mutagenesis by 9,10-anthraquinone derivatives and related Compounds in Salmonella typhimurium." Mutation Research, 40: 203-224.

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